The electronic structure of ordered binary Co–Pt compounds

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Abstract. In this article we present the results of spin-polarized band-structure calculations on the ordered binary compounds of Co–Pt. Comparison is made with experimental values for the magnetic moments. The results of our calculations show a non-local magnetic moment behaviour in these systems. Furthermore we find an almost constant number of holes in the Pt 5d band for the different compounds. The nature of the magnetic interactions is investigated. The coupling between the Co atoms can be described with the Heisenberg Hamiltonian and the exchange coupling parameters are evaluated. With these exchange parameters we are able to calculate the Curie temperature of ordered and disordered Co–Pt alloys.

1. Introduction

The understanding of the magnetic and electronic properties of binary magnetic metallic alloys forms a wide field of research. The study of these systems is interesting not only from a fundamental point but also from a practical point. Among the alloys of the ferromagnetic 3d transition metals and paramagnetic 5d elements the alloys based on platinum have attracted much attention (Kouvel 1967) because of the interesting magnetic and electronic properties of these systems. Alloys of platinum with small concentrations (about 1 at.%) give rise to so-called giant-moment systems (Low 1969), in which the local moments in the alloys exceed considerably the normal values found in the ferromagnetic 3d materials themselves. Another item of interest is the dependence of the electronic and magnetic properties on the composition and crystal structure of the alloys. It is known that there is a close interplay between the magnetic behaviour of these systems and the chemical ordering. The magnetic properties of the ordered binary alloys based on platinum have been studied extensively. The electronic structures have been investigated to a lesser extent. A large variety of magnetic structures is found in these systems (Kouvel 1967). Paramagnetic behaviour is observed in $TiPt_3$, whereas VPt_3 is ferromagnetic although the constituting elements are non-magnetic. Various Pt alloys of one 3d element can show different magnetic orderings, as can be seen in the system Cr–Pt. An antiferromagnetic alignment of the moments is found in $CrPt_3$, whereas CrPt is ferrimagnetic.

In this article we focus on the ordered binary alloys of platinum with cobalt. The phase diagram (Leroux *et al* 1988, Leroux 1989, Sanchez *et al* 1989) of the Co–Pt system shows a FCC structure with a degree of atomic disorder which increases with increasing temperature. Three ordered phases are known at lower temperatures with the stoichiometric compositions Co_3Pt, CoPt and $CoPt_3$. The ordered phases have cubic symmetry of $L1_2$ type for Co_3Pt and $CoPt_3$ and tetragonal symmetry of $L1_0$ type for CoPt. Multilayered structures of Co/Pt, as prepared by MBE techniques, have been studied recently. Magnetic anisotropy and magneto-optical polar Kerr effect measurements were recently performed on vapour-deposited Co/Pt multilayers by Zeper *et al* (1989). These Co/Pt layered structures are promising candidates for reversible information storage based on magneto-optical technology. In this context it is worthwhile noting that the ordered CoPt phase, with Co on the corners and Pt in the centre of the tetragonal unit cell has alternating planes of Co and Pt in the [001] direction and therefore this phase can be considered as a (1:1) multilayer structure of Co and Pt. This ordered CoPt phase is one of the hardest permanent magnets known (Hadjipanayis and Gaunt 1979), especially with respect to coercivity H_c which can reach values of up to 5000 Oe depending on the aging process. The chemical ordering and magnetic properties of the Co–Pt system have been extensively studied (Leroux *et al* 1988, Sanchez *et al* 1989). Both the ordered CoPt and $CoPt_3$ phases are paramagnetic at high temperatures and become ferromagnetically ordered at lower temperatures. Only quite recently the lattice parameter of the ordered Co_3Pt phase with cubic symmetry was determined (Celveyrac 1990). It is assumed that the fully ordered phase shows the same ferromagnetic behaviour as the disordered form (Leroux 1989). $CoPt_3$ has a Curie temperature T_C of approximately 290 K (Leroux 1989). The magnetic moments on Co and Pt in $CoPt_3$, as determined by Menzinger and Paoletti (1966) with neutron diffraction measurements, are $\mu(Co) = 1.64\mu_B$ and $\mu(Pt) = 0.26\mu_B$. The saturation magnetization, determined by bulk-magnetization measurements, is $M_s = 2.43\mu_B$ per unit cell. Ordered CoPt has a T_C of approximately 710 K (Leroux 1989). The saturation magnetization, as determined by van Laar (1964), is $M_s = 1.90\mu_B$ per unit cell. Neutron diffraction measurements show a magnetic moment on both types of atom. van Laar assumed the moment on the Pt atoms to be larger than $0.3\mu_B$ and the moment on the Co atoms to be smaller than $1.6\mu_B$, whereas measurements done by Cable, as discussed in the same article by van Laar (1969), show a moment of $0.25\mu_B$ on Pt and about $1.7\mu_B$ on Co. The T_C and magnetic moments of ordered Co_3Pt have not been determined experimentally.

The electronic structure of Co–Pt intermetallic compounds has not been studied very extensively. The only electronic structure calculations performed so far on these ordered compounds are the tight-binding calculations of Tohyama *et al* (1989) for $CoPt_3$ and Ohta *et al* (1989) for CoPt. In this paper we present the results of *ab initio* spin-polarized self-consistent band-structure calculations of the ordered phases of the binary Co–Pt system. We find qualitatively similar results compared with the calculations done by Tohyama *et al* (1989) and Ohta *et al* (1989), but important quantitative differences. The band structures show a typical alloy-like behaviour with only a little charge transfer between Pt and Co atoms. The calculations reveal that there is an appreciable spin polarization of the Pt atoms in all three ordered alloys, which cannot be accounted for by the simple hybridization of non-magnetic Pt states with magnetic Co states alone. Furthermore we calculated the electronic low-temperature specific heat capacity coefficient γ, which is determined by the density of states (DOS) at the Fermi level.

This investigation is part of a wider study of the magnetic and electronic characteristics of Co/Pt multilayers. The results of the investigations on the binary compounds

form the necessary ingredient for understanding the observed physical properties of these Co/Pt multilayers. Specifically in order to obtain some insight in the magnetic interactions, and also of importance in higher Co/Pt multilayer structures, we performed band-structure calculations on several Co–Pt structures with different hypothetical types of magnetic ordering.

For the description of the nature of the magnetic moments in ferromagnetic metals and alloys, especially for those containing elements from the late 3d series, several models have been proposed (Herring 1966). These models are based on either of the two rival pictures, namely the Heisenberg localized spin model and the Stoner model for the description of itinerant or band magnetism. In the localized model each electron is assumed to remain localized on an atom and, in this way, well localized moments S_i result owing to large intra-atomic electron correlations. The interatomic exchange interactions are much smaller and compete with thermal disorder. The magnetic order can be described by the familiar Heisenberg spin Hamiltonian

$$H = -\sum_{i,j} J_{ij} S_i \cdot S_j. \tag{1}$$

In the Stoner or band model the carriers, either electrons or holes responsible for the magnetism, are itinerant and the interactions between the carriers are described in the mean-field approximation. The exchange splitting of spin-up and spin-down bands leads to the ferromagnetic properties.

Although a wide variety of theoretical contributions incorporating both itinerancy and correlations have been put forward to refine the two extreme models in order to correct the shortcomings of the two models (Moriya 1985) the two theories fail to give a good description of all observed magnetic properties of the system. In the Stoner model no easy description can be given of the magnetic properties above T_C, whereas in the Heisenberg model it is not possible to take into account the dependence of the magnitude of the magnetic moment on chemical environment and magnetic ordering. Kübler *et al* (1983) showed that, even when the electrons responsible for the magnetic properties are delocalized as in the strongly covalent Heusler alloys, the Heisenberg Hamiltonian still applies, as long as the moments are of a localized nature. These workers stress the point that a more basic prerequisite for using the Heisenberg Hamiltonian is that the moments remain constant when their direction is reversed. As will be shown, the moments in CoPt are not the same for the various magnetic structures. Nevertheless we shall show that it is possible to describe the magnetic structures of the ordered CoPt alloy with a few exchange coupling parameters, even when the magnetic moments for the different magnetic moment alignments are allowed to differ appreciably from the ferromagnetic structure. From the energy differences between the ferromagnetic and the various antiferromagnetic alignments of the Co moments we determined the exchange coupling parameters J_i.

In ferromagnetic metals and alloys, several exchange mechanisms have to be considered. In 1:1 Co:Pt we have, besides the direct exchange due to direct overlap of the d orbitals of Co, also other exchange mechanisms. Interaction between the Co magnetic moments via the intermediate Pt atoms (so-called superexchange) is caused by hybridization of the Co d orbitals with (mainly) the Pt d orbitals. Furthermore there is an indirect exchange whereby the coupling between the Co spins is mediated through the sea of conduction electrons, formed mainly by the Co and Pt s and p electrons. If strong hybridization occurs between the conduction electrons and magnetic electrons, the effects of indirect and superexchange cannot be well separated. Therefore the coupling

parameters are to be seen as weighted averages and give only an idea of the strength of exchange coupling of the Co atoms in the same plane and between successive Co layers in CoPt.

2. Details of the calculation

Self-consistent band-structure calculations were performed using the localized-spherical-wave (LSW) method. This is a variational method which determines a self-consistent solution of the single-particle Schrödinger equation within the local-density approximation. The solution of this eigenvalue problem is expanded in a basis set, the so-called LSWs. Apart from a transformation of the basis set to obtain the most localized muffin-tin orbitals, as first suggested by Andersen and Jepsen (1984), the localized spherical waves are equivalent to the augmented spherical waves (ASWs) in the well known ASW method, as described by Williams *et al* (1979). For more quantitative details about the construction of the basis set in the LSW method we refer to the article of van Leuken *et al* (1990). Scalar relativistic effects (mass–velocity and Darwin terms) were included as described by Methfessel and Kübler (1982). The local exchange–correlation potential of von Barth and Hedim (1971) was used. The self-consistent calculations were carried out including all core electrons. The LSW as well as the ASW method employs the atomic sphere approximation (ASA). In this approximation the crystal is subdivided into overlapping Wigner–Seitz spheres, centred around each atomic position in the unit cell and with a total volume that equals the volume of the unit cell. It is therefore understandable that this method is most suited to those materials and compounds that are densely packed. The Co–Pt compounds studied here are close-packed structures and can therefore be well described by this method. A word of precaution is necessary when interpreting those results of the band-structure calculations which are dependent on the choice of the Wigner–Seitz radius R_{WS}, e.g. the magnitudes of the magnetic moments and charge transfer. In order to be able to compare the magnetic moments of Co and Pt in the different compounds, we have chosen the Wigner–Seitz radius for Co for the different compounds as in bulk hexagonal α-Co, and we adjusted the Wigner–Seitz radius of Pt so as to make the sum of the volumes of the spheres equal to the volume of the unit cell. The crystal structure of Co_3Pt is described by the space group $Pm3m$ O_h^1 (no 221 in the international tables). In the unit cell the Co atoms occupy the 3c sites $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and the Pt atoms occupy the 1a site $(0, 0, 0)$. $CoPt_3$ can be described within the same space group where the Co and Pt atoms occupy the 3c and 1a sites in reverse order. The $(1:1)$ compound CoPt is described by the space group $P4/mmm$ (no. 123 in the international tables) with the Co atoms on the special positions 1a $(0, 0, 0)$ and the Pt atoms on the special positions 1d $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The only input parameters for the calculations were the atomic numbers, the crystal structure (as given above) and the Wigner–Seitz radii. For all compounds we used for the Co atoms the 3d, 4s and 4p functions as basis functions and for the Pt atoms the 6s, 6p and 5d functions. The Co 4f and Pt 5f functions were included in the internal summation of the three-centre contributions to the matrix elements, which can be regarded as treating these functions as a perturbation. The number of atoms inside the screening cluster, for the different positions in the different structures, was 19 for each compound. We used the experimental lattice parameters of Co_3Pt (Celveyrac 1990), CoPt (Newman and Hren 1967) and $CoPt_3$ (Berg and Cohen 1972) as input parameters. These parameters and the

Table 1. Input parameters for the band-structure calculations.

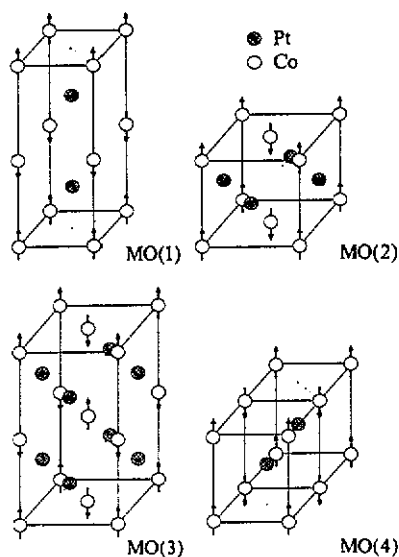|	Space group	a (Å)	c (Å)	R_{WS-Co} (Å)	R_{WS-Pt} (Å)
α-Co	$P6_3/mmc$	2.5071	4.0686	1.383	
Co$_3$Pt	$Pm3m$	3.6636		1.383	1.562
CoPt	$P4/mmm$	2.682	3.675	1.383	1.542
CoPt$_3$	$Pm3m$	3.8540		1.383	1.543
Pt	$Fm3m$	3.9231			1.533
FCC Co	$Fm3m$	3.5447		1.385	

Figure 1. Various hypothetical antiferromagnetic structures of CoPt with magnetic orderings from MO(1) to MO(4).

Wigner–Seitz radii R_{WS} are given in table 1, together with the Wigner–Seitz radii of bulk cubic Pt (Wyckoff 1960) and bulk hexagonal α-Co (Wyckoff 1960).

The crystallographic unit cells which were used for the description of the various hypothetical antiferromagnetic alignments in CoPt are shown in figure 1. The magnetic ordering depicted as MO(1) consists of ferromagnetically ordered planes of Co moments, which are antiferromagnetically ordered along the [001] direction. This structure is described by the (crystallographic) space group $P4/mmm$ (no. 123) where the two inequivalent Co atoms occupy the special positions 1a $(0, 0, 0)$ and 1b $(0, 0, \frac{1}{2})$ and the non-magnetic Pt atoms occupy the special positions 1h $(\frac{1}{2}, \frac{1}{2}, z)$ with $z = \frac{1}{4}$. In the magnetic structures depicted as MO(2) and MO(3) the Co atoms are antiferromagnetically aligned in the planes, with alternating spin orientations along the [110] direction. The ordering of the planes in MO(2) is such that neighbouring atoms along the c direction are ferro-magnetically coupled, while in the case of the magnetic structure MO(3) this coupling is antiferromagnetic. The latter configuration leads to a doubling of the unit cell along the c direction, compared with the ferromagnetic case. The structure MO(2) is described by the same space group $P4/mmm$ where the two inequivalent Co atoms occupy the special
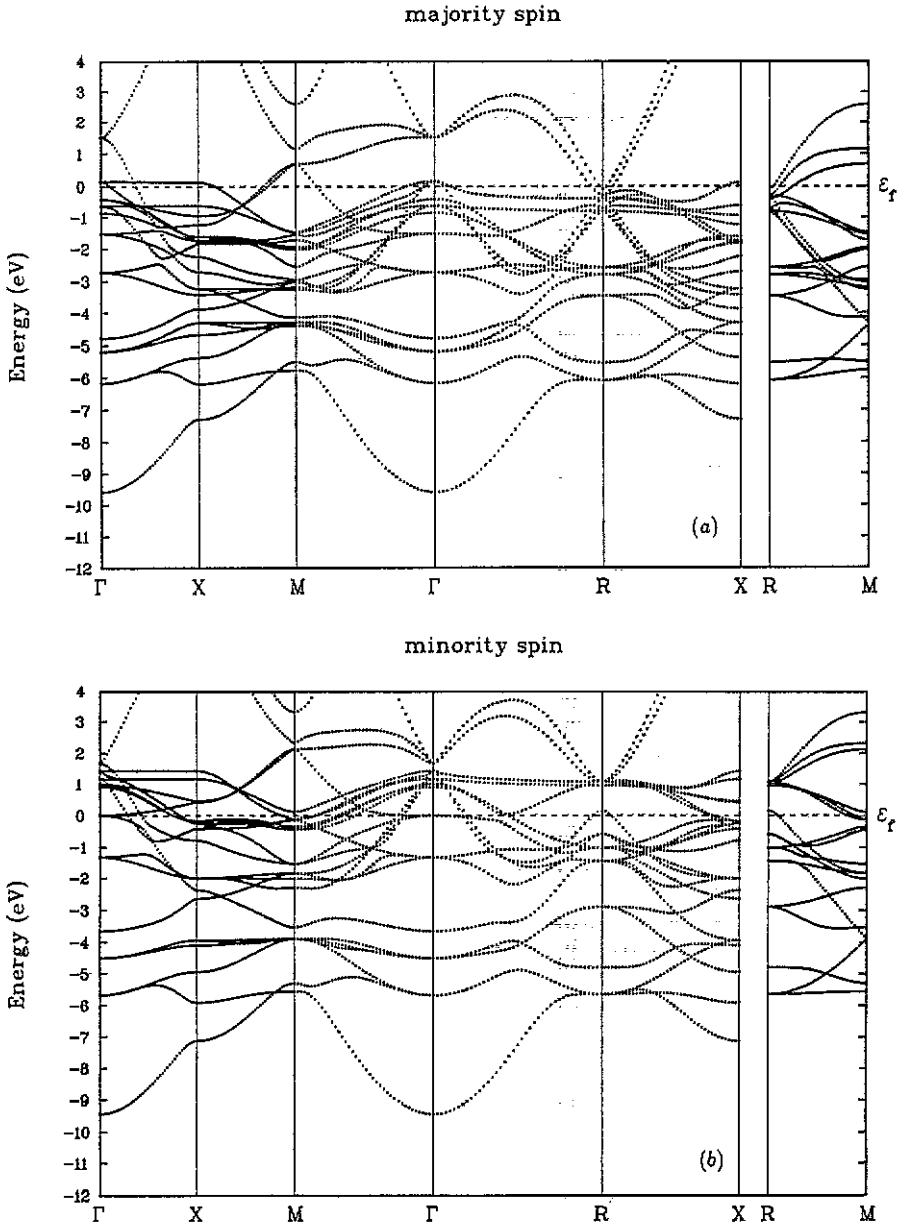
majority spin

minority spin

Figure 2. Calculated electronic energy bands of ferromagnetic Co_3Pt along high-symmetry lines for (*a*) the majority spin direction and (*b*) the minority spin direction.

positions 1a $(0, 0, 0)$ and 1c $(\frac{1}{2}, \frac{1}{2}, 0)$ and the Pt atoms occupy the positions 2e $(\frac{1}{2}, 0, \frac{1}{2})$. The structure MO(3) is described by the space group $I4/mmm$ (no. 139). In the body-centred unit cell the two inequivalent Co atoms occupy the sites 2a $(0, 0, 0)$ and 2b $(0, 0, \frac{1}{2})$ and the Pt atoms occupy the special positions 4d $(0, \frac{1}{2}, \frac{1}{4})$. In the magnetic structure depicted as MO(4) we have a doubling of the unit cell in the basal plane, in which

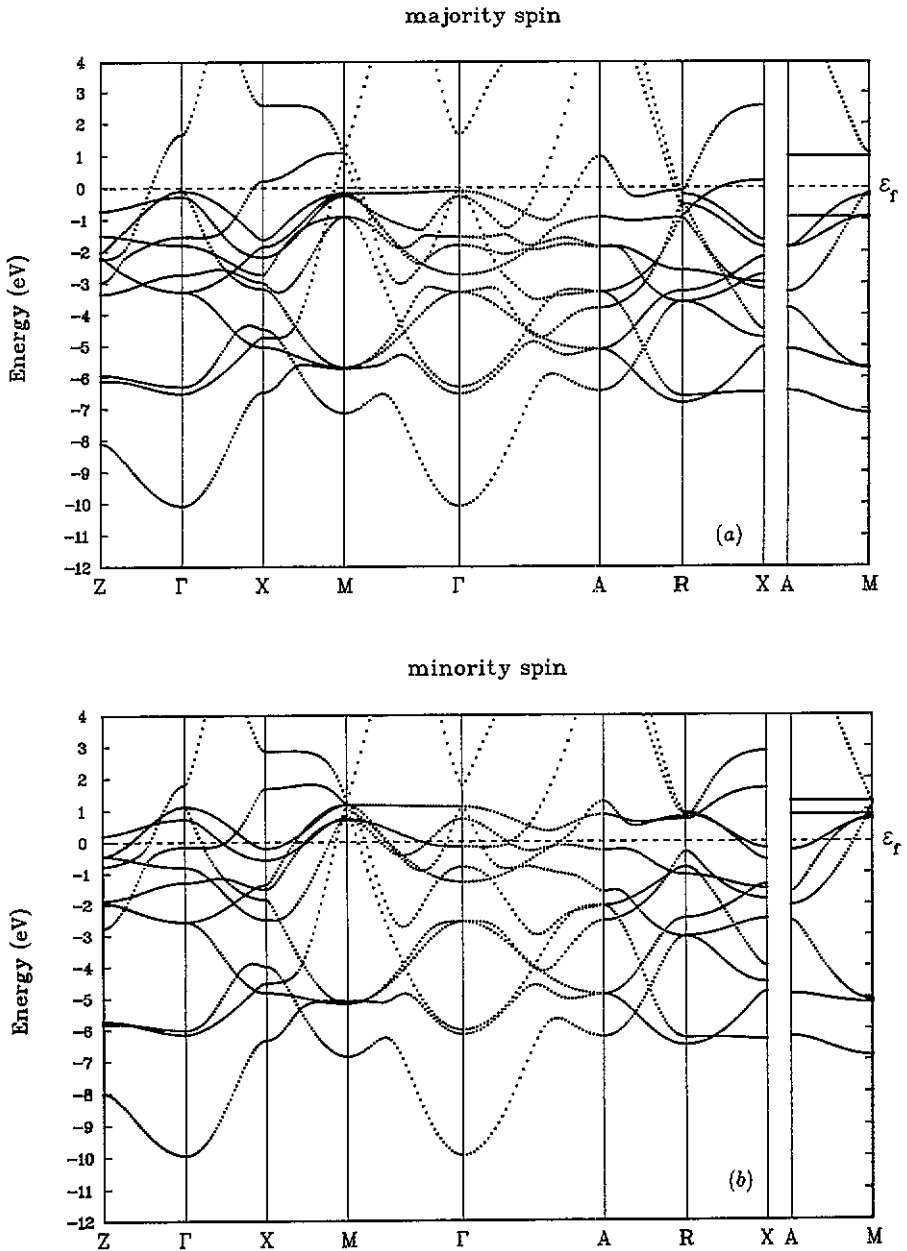majority spin

minority spin

Figure 3. Calculated electronic energy bands of ferromagnetic CoPt along high-symmetry lines for (a) the majority spin direction and (b) the minority spin direction.

the Co atoms are antiferromagnetically coupled, whereas the planes along the [001] direction are ferromagnetically coupled. This structure is described by the orthorhombic space group *Pmmm* (no. 47). In the unit cell the two inequivalent Co atoms occupy the special positions 1a $(0, 0, 0)$ and 1b $(\frac{1}{2}, 0, 0)$ and the Pt atoms occupy the special positions 2l $(x, \frac{1}{2}, \frac{1}{2})$ with $x = \frac{1}{4}$.
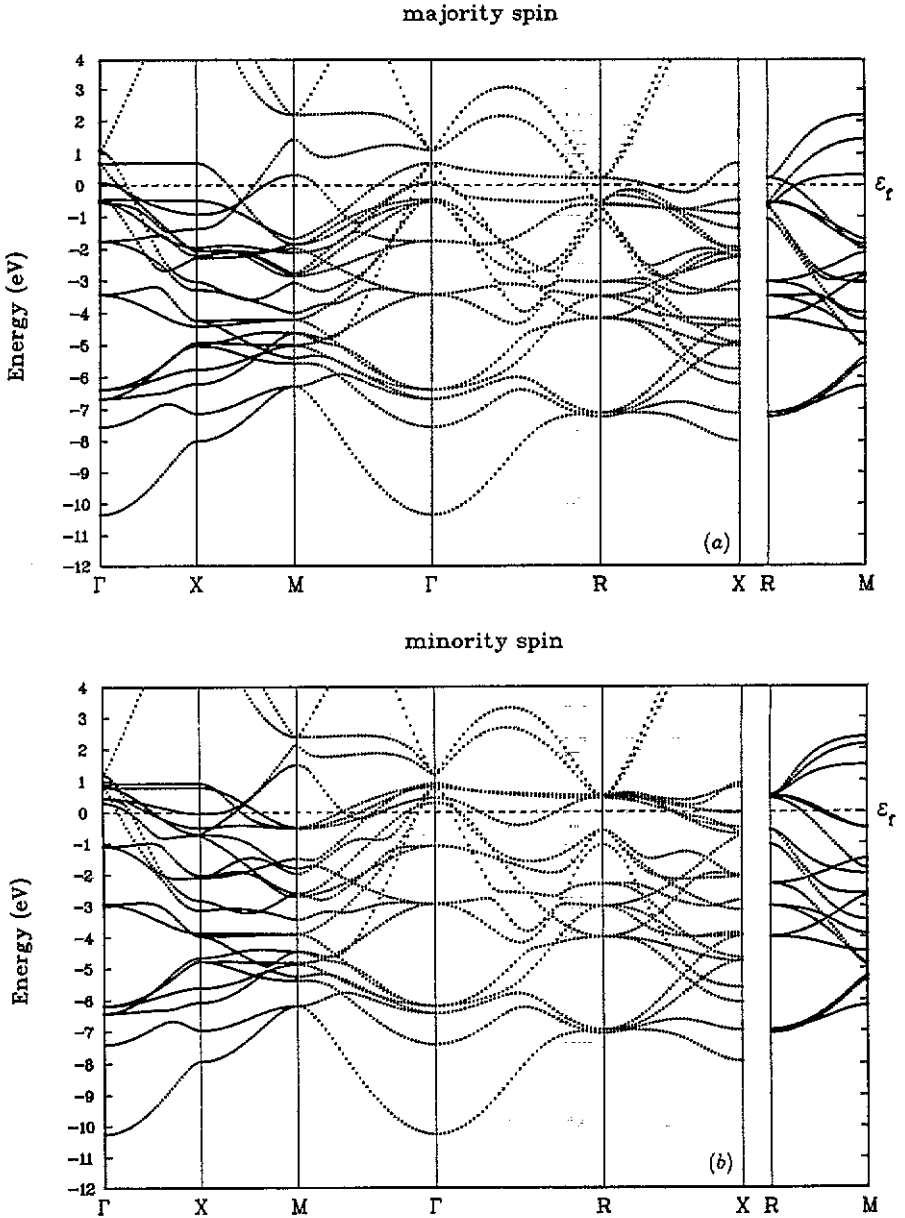
majority spin

minority spin

Figure 4. Calculated electronic energy bands of ferromagnetic CoPt$_3$ along high-symmetry lines for (a) the majority spin direction and (b) the minority spin direction.

The calculations were carried out until self-consistency was obtained. Iterations were performed with the k-points uniformly distributed in the irreducible part of the first Brillouin zones corresponding to a volume of reciprocal space of the order of 10^{-5} Å^{-3} per k-point. The total DOS and the atomic-site- and angular-momentum-resolved DOS were derived from the band energies on a regular mesh in the irreducible part of the Brillouin zone with a k-point mesh density of the order of 5×10^{-6} Å^{-3} using energy
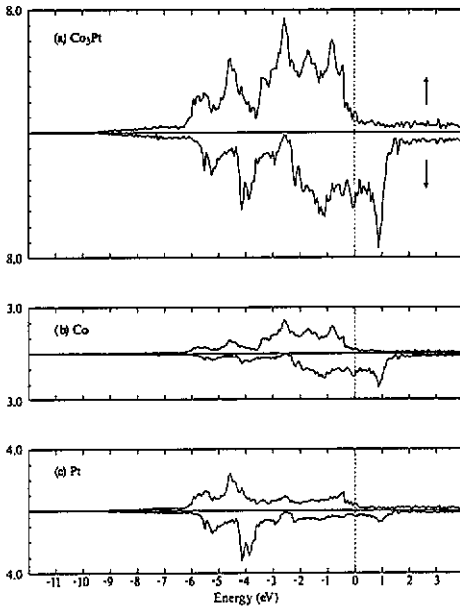
Figure 5. Spin- and site-projected DOSs of ferromagnetic Co₃Pt, with (*a*) the total DOSs in states per electronvolt per unit cell, (*b*) the partial DOS at the Co site and (*c*) the partial DOS at the Pt site in states per electronvolt per atom.
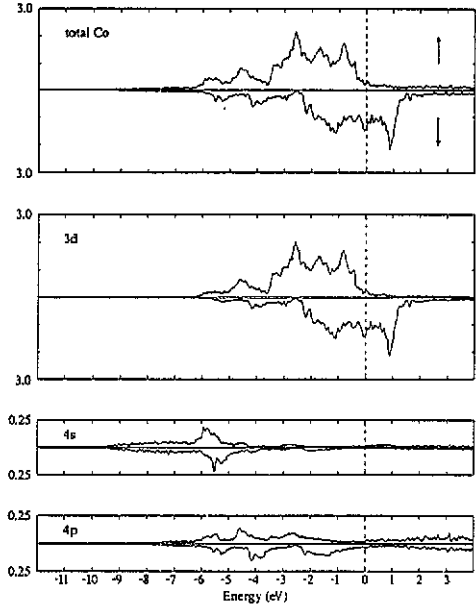
Figure 6. Spin- and angular-momentum-resolved DOS of Co₃Pt at the Co site in states per electronvolt per atom.

intervals of about 5 mRyd. Self-consistency was assumed when the changes in the local partial charges in each atomic sphere decreased to the order of 2×10^{-5}. We also carried out band-structure calculations for Co and Pt using the LSW method. Two phases of Co are known. The HCP phase (α-Co) with hexagonal crystal structure is stable at temperatures below about 640–700 °C. A phase transition from HCP to FCC occurs at about 750 °C. Experimentally, FCC Co may be stabilized by rapid quenching. The results are in good agreement with calculations reported in the literature for α-Co and FCC Co (Min *et al* 1986) and Pt (Andersen 1970).

3. Results of the calculations

3.1. Ferromagnetic Co₃Pt, CoPt and CoPt₃

The calculated energy bands of Co₃Pt, CoPt and CoPt₃ for both spin directions are displayed in figures 2, 3 and 4, respectively. The energy as a function of wavevector *k* is plotted along high-symmetry lines in the Brillouin zones, using the symmetry notations of Miller and Love (1967). When we compare the band structures of Co₃Pt and CoPt₃ we observe similarities in certain *k*-directions. CoPt has a quite distinct structure owing to the lower symmetry. No simple assignment of bands to either Co or Pt states can be performed, because of the strong hybridization between Co and Pt states over the whole energy range, which is typical for an alloy. The bands at lower energy, lower than about
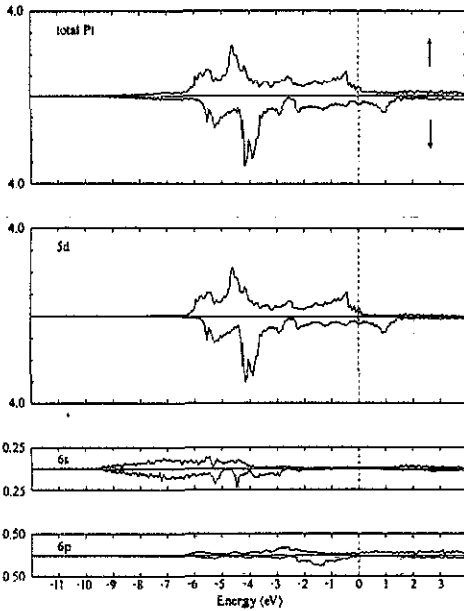
Figure 7. Spin- and angular-momentum-resolved DOS of Co₃Pt at the Pt site in states per electronvolt per atom.
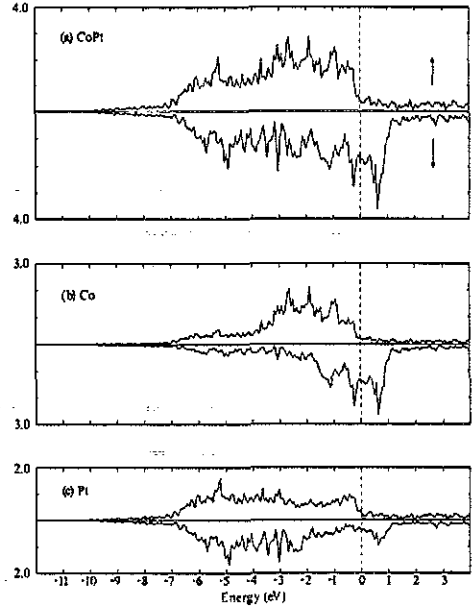
Figure 8. Spin- and site-projected DOS of ferromagnetic CoPt, with (a) the total DOS in states per electronvolt per unit cell, (b) the partial DOS at the Co site in states per electronvolt per atom and (c) the partial DOS at the Pt site in states per electronvolt per atom.

−7 eV, are of predominantly s character and are of strongly Co/Pt mixed nature. The bands above −7 eV are predominantly of d character and also show a large hybridization, in this case between the Pt 5d and Co 3d states. In figures 5–13 the total DOS and the site-projected DOS at the Co and Pt site in Co₃Pt, CoPt and CoPt₃ are shown. The partial DOS resulting from the 4f level of Co and 5f level of Pt are omitted, because their contribution is negligibly small. Further insight regarding the nature of the bonding in these compounds can be obtained by considering the decomposition into angular momentum contributions of the charge inside each Wigner–Seitz sphere, as shown in figures 5–13 and given in table 2.

As is observed in table 2 the number of electrons or equivalently the number of holes in the Co 3d as well as in the Pt 5d bands for majority and minority spin remains almost constant. There are about 0.4 and 2.1 holes for majority and minority spin direction in the Co 3d band and about 0.6–0.7 and 1.1 holes in the Pt 5d band. It is interesting to perform measurements of x-ray absorption or spin-polarized photoelectron spectroscopy in order to determine experimentally the occupation of the Pt d bands. Preliminary results have been reported by Schütz et al (1990). We note that the largest contribution to the calculated moment on the Pt atoms comes from the 5d electrons and a minor contribution is given by the 6p electrons.

The strong hybridization of the Co 3d and Pt 5d levels is clear from the total DOS plots and even more from the partial DOS per atomic site in each compound. The large exchange splitting at the Co site for the 3d level in each compound as we expect should
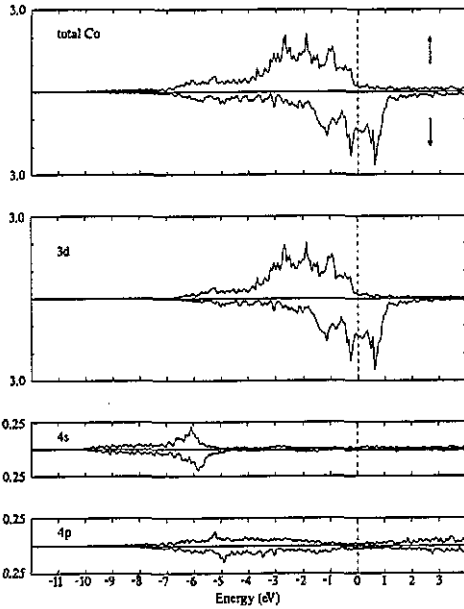
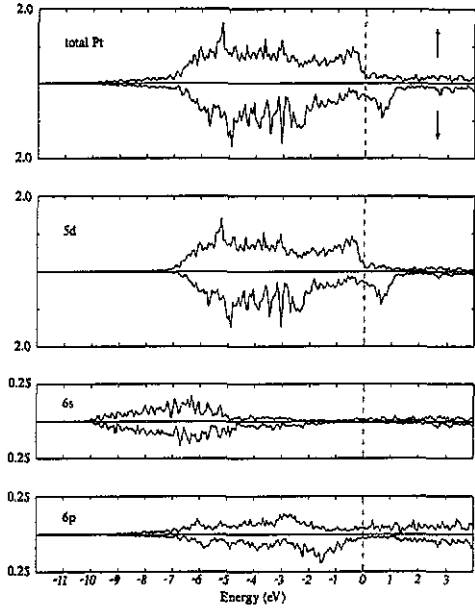**Figure 9.** Spin- and angular-momentum-resolved DOS of CoPt at the Co site in states per electronvolt per atom.

Figure 10. Spin- and angular-momentum-resolved DOS of CoPt at the Pt site in states per electronvolt per atom.

Figure 11. Spin- and site-projected DOS of ferromagnetic CoPt₃, with (*a*) the total DOS in states per electronvolt per unit cell, (*b*) the partial DOS at the Co site in states per electronvolt per atom and (*c*) the partial DOS at the Pt site in states per electronvolt per atom.

Figure 12. Spin- and angular-momentum-resolved DOS of CoPt₃ at the Co site in states per electronvolt per atom.

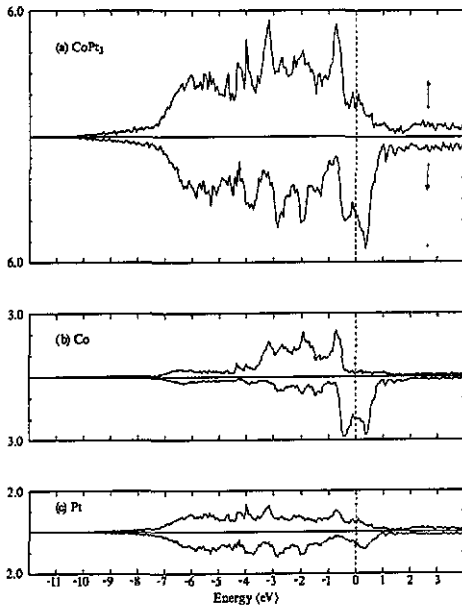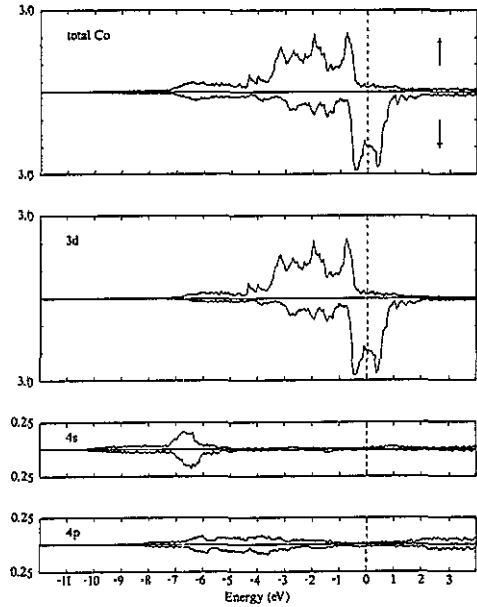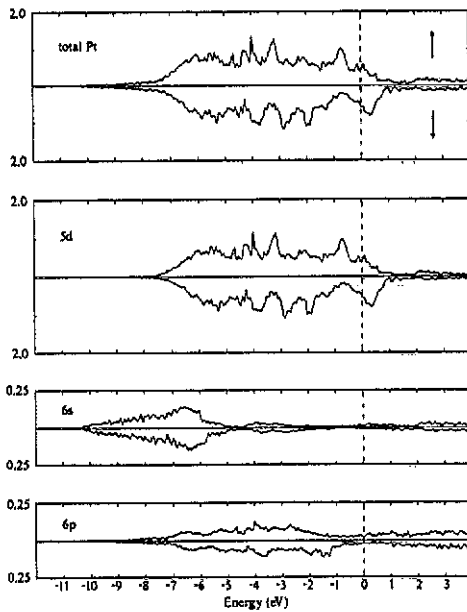Figure 13. Spin- and angular-momentum-resolved DOS of CoPt$_3$ at the Pt site in states per electronvolt per atom.

Table 2. Total charge decomposition for Co and Pt into different angular momentum components for the ordered alloys of Co–Pt for majority and minority spin directions.

	Charge decomposition (electrons/atom)								
	Co$_3$Pt		CoPt		CoPt$_3$		α-Co		Pt
	Majority	Minority	Majority	Minority	Majority	Minority	Majority	Minority	per spin
Co 3d	4.59	2.92	4.61	2.91	4.61	2.93	4.59	2.95	
4s	0.30	0.31	0.29	0.29	0.27	0.27	0.32	0.33	
4p	0.34	0.37	0.34	0.35	0.32	0.32	0.35	0.41	
4f	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.03	
Pt 5d	4.37	3.93	4.34	3.91	4.28	3.98			4.14
6s	0.45	0.47	0.42	0.43	0.40	0.41			0.38
6p	0.44	0.52	0.43	0.48	0.42	0.45			0.41
5f	0.07	0.06	0.07	0.06	0.07	0.07			0.07

be noted and also the majority spin 3d bands which are almost completely filled. The tail in the Co 3d DOS at higher energies above ε_F is a result of hybridization with the underlying broad s and p bands of Co and Pt. The partial DOS of the Co 4s level shows a maximum at about -6.5 eV for Co$_3$Pt, -6 eV for CoPt and about -5.5 eV for CoPt$_3$. The maximum occurs in all cases at the bottom of the d bands which consist mainly of Pt 5d contributions. Therefore we ascribe this maximum to hybridization of Co 4s orbitals with the d band. The calculations that we carried out for FCC and HCP Co show

Table 3. Calculated and experimental values of the magnetic moments, the saturation magnetization M_s and the charge transfer from Co to Pt, together with the total DOS $D(\varepsilon_F)$ at the Fermi level in the ordered compounds of Co–Pt alloys.

		μ_{Co} (μ_B)	μ_{Pt} (μ_B)	M_s (μ_B/unit cell)	$D(\varepsilon_F)$ (states eV^{-1}/unit cell)	Charge transfer (electrons/Co atom)
Co$_3$Pt	Calculated	1.64	0.36	5.28	6.10	0.10
CoPt	Calculated	1.69	0.37	2.06	2.20	0.14
	Experimental[a]	≈1.7	≈0.25	1.90		
CoPt$_3$	Calculated	1.69	0.27	2.50	5.11	0.22
	Experimental[b]	1.64	0.26	2.43		
Pt	Calculated				1.93	
α-Co	Calculated	1.57		3.14	1.70	
	Experimental[c]	1.58				
FCC Co	Calculated	1.61		1.61	1.27	
	Experimental[d]	1.61				

[a] From van Laar (1964).

[b] From Menzinger and Paoletti (1966).

[c] From Meyers and Sucksmith (1951).

[d] From Crangle (1955).

a less pronounced maximum in the 4s DOS at an energy near the bottom of the Co 3d band. When we look at the partial DOS at the Pt site, we see that the exchange splitting of the Pt 5d level is much less than that of Co. The Pt partial DOS for CoPt and CoPt$_3$ are very similar to bulk cubic Pt, whereas there is a pronounced difference for Co$_3$Pt. The partial DOS of the 5d level in Co$_3$Pt shows a sharply peaked structure at around -4.5 eV for majority spin and at around -4 eV for minority spin. These maxima are due to the pair of rather flat bands at this energy in the direction from X to M, as can be seen in figures 2(a) and 2(b). A wavefunction analysis has shown that these bands have predominantly Pt 5d character. These states are of more localized character than in bulk Pt and therefore show a more peaked structure in the resulting DOS because there are no nearest-neighbour Pt–Pt interactions in Co$_3$Pt.

In table 3 the magnetic moments on the Co and Pt site of the different compounds, obtained from the difference of spin-up and spin-down charge within each Wigner–Seitz sphere, are given, together with the value of the total magnetization M_s per unit cell (in Bohr magnetons per unit cell). As noted before, these quantities depend slightly on the atomic radii chosen but, because we chose the radius of the Co atom to be constant, a comparison of the values for the different compounds is useful. Also given are the values of the charge transfer from Co to Pt (in electrons per atom).

Each compound shows a small charge transfer from Co towards Pt, which is in agreement with the difference between the electronegativities of the two elements. The calculated magnetic moment on Co in the Co–Pt compounds of about $1.7\mu_B$ is somewhat larger than the value for bulk α-Co, but it is essentially the same in the three compounds. The Pt atoms are strongly spin polarized by the Co atoms and acquire an induced moment of about $(0.3–0.4)\mu_B$. The moment on the Pt atoms is a result of the high magnetic polarizability of the Pt atoms. The Co spin induces magnetic moments on the Pt neighbours, an effect also seen in dilute Co–Pt alloys. As already mentioned in the introduction, a small amount of Co dissolved in Pt results in a so-called giant-moment system

in which half of the apparent moment of $3.6\mu_B$ is attributed to the Co impurity ($1.7\mu_B$) and half to the polarization of Pt neighbours (see, e.g., Ododo 1982). The calculated values for the magnetic moments in CoPt and $CoPt_3$ are in excellent agreement with the values for the ordered compounds as determined by neutron diffraction. Sanchez *et al* (1989) determined the saturation magnetization of $Co_{1-x}Pt_x$ alloys as function of concentration x by magnetization measurements. These workers calculated the magnetic moment on Pt using the assumption that the magnetic moment of Co remains the same as it is in bulk Co. The values obtained in this way lead to a marked decrease in the magnetic moment on Pt with increasing Pt content. Our calculations show no evidence for such a strong decrease. A remarkable fact is that the magnetic moment induced on Pt is nearly the same for all these Co–Pt compounds. Apparently the induced moment is not enhanced by the presence of more magnetic Co neighbours. Moreover, also in other magnetic Pt compounds (VPt_3 and $CrPt_3$) the induced moment on Pt is nearly the same (Tohyama *et al* 1989). This indicates that an induced moment of $0.37\mu_B$ corresponds to a saturation which cannot be enhanced easily. The moment of $0.37\mu_B$ agrees fairly well with the number of holes (0.40) in the Pt 5d band (Anderson 1970).

From the total DOS $D(\varepsilon_F)$ at the Fermi level (in units states per electronvolt per unit cell) we calculated the electronic specific heat coefficient γ, which is given by the relation

$$\gamma = \tfrac{1}{3}\pi^2 k_B^2 D(\varepsilon_F). \tag{2}$$

We found for γ (per mole atom) for Co_3Pt a value of $3.59\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$, for CoPt $2.59\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ and for $CoPt_3$ $3.01\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$. The experimental values for CoPt and $CoPt_3$ are 5.16 and $6.1\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$, reported by Küntzler (1981). The calculated values of γ for bulk α-Co and Pt are $2.01\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ and $4.56\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$, whereas the experimental values for α-Co and Pt are $4.73\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ (Cheng *et al* 1960) and $6.56\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ (Shoemake and Rayne 1968), respectively. We believe the deviation between the calculated and experimental values of γ is mainly due to mass enhancement because of electron–phonon interaction.

Finally we compare our results with calculations of the band structure of TPt and TPt_3 ordered alloys (T $\equiv$ 3d transition metal) (Tohyama *et al* 1989, Ohta *et al* 1989). These are tight-binding calculations of Pt 5d and T 3d bands only. The calculations are self-consistent, but semi-empirical, in that assumptions are made for the number of d electrons per atom and for the intra-atomic Coulomb energy. The calculations predict in most cases the correct type of magnetic order. However, for $MnPt_3$ the calculations predict antiferromagnetism, whereas ferromagnetism is observed. The calculated values of the Pt magnetic moments vary between $0.20\mu_B$ and $0.40\mu_B$. The values obtained for the Pt magnetic moment in CoPt and $CoPt_3$ are $0.34\mu_B$ and $0.38\mu_B$, respectively, in good agreement with the values obtained by us. However, the values obtained for the Co magnetic moments of $1.93\mu_B$ (CoPt) and $2.88\mu_B$ ($CoPt_3$) deviate strongly from the experimental values and from our calculated value. The DOS curves reported in the tight-binding calculations show general agreement with our results with regard to width and position of Co and Pt d bands. However, there are also significant differences. For example, the pronounced maximum in the DOS for spin-down electrons for CoPt at $0.8\,\mathrm{eV}$ above ε_F lies in the calculations by Ohta *et al* (1989) just at ε_F.

3.2. *Magnetic interactions in CoPt*

To gain more insight into the nature of the exchange interactions in CoPt, we calculated the electronic structure of several hypothetical magnetic structures with an anti-ferromagnetic alignment of the Co moments, as is shown in figure 1. The electronic

Table 4. Energy δE per Co site of the various antiferromagnetic magnetic structures, the ferromagnetic structure and non-magnetic structure MO(2), together with the moments on the Co atoms.

	Value for the following structures				
	Ferromagnetic	MO(1)	MO(2)	MO(3)	MO(4)
δE (meV/site)	−165.6	−137.7	0	−62.7	−85.5
μ(Co) in μ_B	1.69	1.63	0	1.37	1.47

structure of these magnetic alignments can be calculated if one uses the constraint that the majority spin density at a cobalt site is symmetry equivalent to the minority spin density on another cobalt site, which is crystallographically equivalent but with an opposite magnetic moment. Although this can be implemented in a straightforward way, no guarantee is hereby made that the system will converge to an antiferromagnetic structure. The system still has the degree of freedom to converge to a non-magnetic state if the energy of this state is lower than the assumed antiferromagnetic state (the same is true, of course, for a ferromagnetic calculation). Indeed we observed during the calculation that the structure MO(2) converged to a non-magnetic state and the moments on Co disappeared very slowly during the iteration process. Although such behaviour is possible, it occurs only seldom in practice. Because of symmetry no moment was found on the Pt atoms in any of the antiferromagnetic structures.

In table 4 we have given the calculated energy differences of the various antiferromagnetic structures MO(i) and the ferromagnetic structure with respect to the non-magnetic state MO(2). In this way we consider only the magnetic contribution to the total energy. Also shown are the calculated magnetic moments on the Co atoms.

It is found that all antiferromagnetic structures lie at higher energy compared with the ferromagnetic ground state. As can be seen from table 4, the moments show appreciable differences in the various magnetic structures, which is an indication of the non-locality of the magnetic moments in CoPt. The value of the magnetic moment increases with increasing stability of the magnetic ordering. Thermal variations in reciprocal paramagnetic susceptibilities of both ordered and disordered Co–Pt alloys as measured by Dahmani (1985) show Curie–Weiss-type behaviour. According to Rhodes and Wohlfarth (1963) the comparison of the effective or paramagnetic moment q_c, which can be deduced from the Curie–Weiss constant C_m, with the saturation moment q_s in the ferromagnetic state gives qualitative information about the degree of localization of magnetism. High values of the ratio q_c/q_s are found for weak ferromagnetic materials and the limiting value of unity is found for materials with strongly localized magnetic moments. In this way, Leroux *et al* (1988) find strong, nearly localized ferromagnetic behaviour for CoPt. However, our calculations show a dependence of magnetic moment on the magnetic structure which can be explained only if the wavefunctions of the electrons responsible for the observed magnetic behaviour (mainly the 3d electrons of Co) show appreciable overlap.

A remarkable result is the strong variation in the magnetic moment with the type of ordering and the total loss of magnetization in the structure MO(2). We analyse this behaviour in terms of a series expansion of the energy:

$$\delta E_i = -A_i S^2 + B_0 S^4 + C_0 S^6 + \dots \tag{3}$$

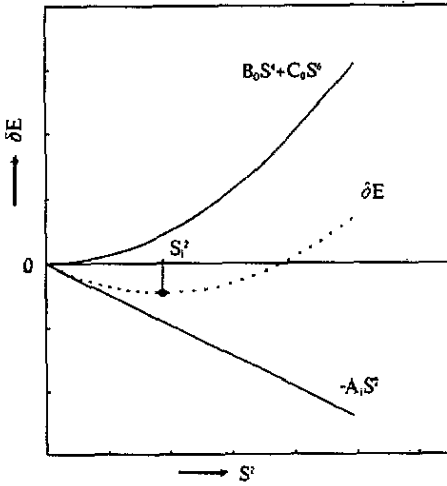A similar expression is used in theories of itinerant magnetism (the Stoner model (see,

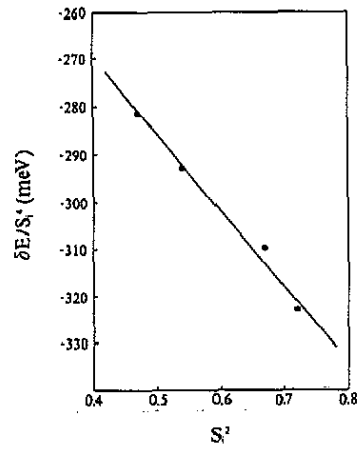Figure 14. Magnetic energy as a function of the spin S.

Figure 15. Plot of $\delta E_i / S_i^4$ versus S_i^2.

e.g., Moriya 1985)). There are several contributions to the magnetic energy δE_i. First there is the intra-atomic exchange energy, which describes the energy gain due to the formation of a magnetic moment of magnitude S_i. This contribution is quadratic in S_i; it is the main contribution to the Stoner parameter I. There is evidence that this term is nearly independent of the type of magnetic ordering i (Kübler 1980, Stollhoff *et al* 1990). We neglect the energy contribution of the formation of a magnetic moment on the Pt site in ferromagnetic CoPt, since the energy difference between non-magnetic and magnetic Pt can be considered to be small, owing to the high magnetic polarizability of Pt.

The second contribution to δE_i is the band energy, resulting from the change in the distribution of electrons over spin-up and spin-down energy bands as a result of the magnetic moment formation. This contribution is responsible for the interatomic exchange between magnetic moments on the atoms. As far as the energy difference between the magnetic structures i can be described with a Heisenberg Hamiltonian for the interatomic exchange, it will give a contribution to the magnetic energy δE_i which is quadratic in S_i. Therefore we expect that the parameter A_i will depend on the type of magnetic ordering i, whereas the parameters B_0 and C_0 will be independent of i.

The magnetic energy δE_i as a function of S_i^2 is shown in figure 14. For $A_i < 0$ the lowest energy is obtained for the non-magnetic state with $S_i = 0$, $\delta E_i = 0$. For $A_i > 0$ the lowest energy is obtained from $\partial(\delta E_i)/\partial S_i^2 = 0$. From this condition we find that

$$A_i = 2B_0 S_i^2 + 3C_0 S_i^4 \tag{4}$$

and for the minimum energy

$$\delta E_i = -B_0 S_i^4 - 2C_0 S_i^6. \tag{5}$$

We find indeed that calculated values of $\delta E_i / S_i^4$ (from the data given in table 4) as a function of S_i^2 give a straight line (figure 15). From figure 15 we obtain the values $B_0 = 205.2$ meV and $C_0 = 80.6$ meV.

We have also attempted a further analysis of the energies δE_i in terms of a Heisenberg model for interatomic exchange between the Co atoms. For this analysis the following
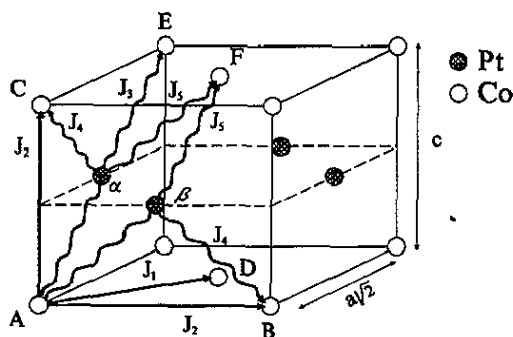
Figure 16. Exchange interactions in CoPt ($\bigcirc$, Co atoms; $\bullet$, Pt atoms): (*a*) direct interactions J_1 ($Co_A–Co_D$) and J_2 ($Co_A–Co_B$ or $Co_A–Co_C$); (*b*) indirect interactions via one intermediate Pt atom: J_3 ($Co_A–Pt_\alpha–Co_E$), J_4 ($Co_A–Pt_\alpha–Co_C$ or $Co_A–Pt_\beta–Co_B$) and J_5 ($Co_A–Pt_\alpha–Co_F$ or $Co_A–Pt_\beta–Co_F$).
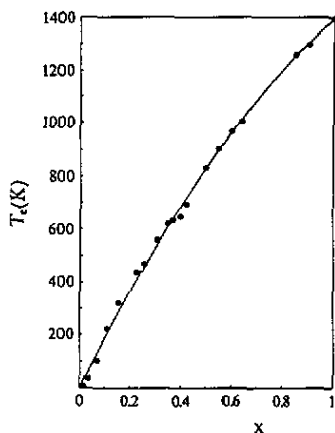
Figure 17. Curie temperatures T_C of disordered ferromagnetic alloys $Co_{1-x}Pt_x$: $\bullet$, experimental data (data from Sanchez *et al* (1989) and Leroux (1989)); ——, calculated with equation (7).

exchange interactions are considered (figure 16). First there are direct Co–Co exchange interactions J_1 between nearest neighbours (at distance a) and interactions J_2 between next-nearest neighbours (at distances $a\sqrt{2}$ or c). The distances between Co atoms along the c axis are slightly different from the corresponding distances in the a–b plane ($c = 3.675$ Å and $a\sqrt{2} = 3.793$ Å). This will generally lead to different values for the exchange interactions. However, it is found experimentally that the Curie temperature of FCC Co metal is nearly independent of pressure (Leger *et al* 1967, Klebanov 1973). This indicates that the variation in the exchange constants with interatomic distance is small. In our considerations, we shall neglect this variation and assume the same value J_2 for direct Co–Co exchange interactions along the c axis and for the corresponding interactions in the a–b plane.

We also consider indirect Co–Co exchange via Pt atoms (figure 16). The first is the 180° indirect exchange interaction J_3 via one intermediate Pt atom. The second interaction is a 90° indirect interaction J_4, also via one intermediate Pt atom (figure 16). Finally we take into account an indirect interaction J_5 via one intermediate Pt over a distance $\sqrt{a^2 + c^2}$ between the Co atoms. It is possible to take into account also exchange interactions via more than one intermediate Pt atom. The theory for such long-range interactions was discussed recently (Geertsma and Haas 1990). There is some evidence (to be discussed later) that these long-range interactions are not very large in Co–Pt alloys.

If the exchange constants are not sensitive to small variations in interatomic distances, it is possible to compare data on the Curie temperature of disordered Co–Pt alloys with the information on the exchange constants deduced from band-structure calculations. The Curie temperature of a disordered $Co_{1-x}Pt_x$ alloy can be written as

$$T_C = [2S(S + 1)f/3k_B][xJ + x(1 - x)J'].\tag{6}$$

In this equation, S is the spin on a Co atom, and f is a factor correcting for the molecular-field approximation (for a FCC structure with only nearest-neighbour interactions, $f =$

0.695 (Domb and Sykes 1957)). The parameter J represents all direct Co–Co interactions, and J' all indirect Co–Co interactions via one intermediate Pt atom. Long-range interactions via more than one intermediate Pt would give rise to terms such as $x(1 - x)^2 J''$ for Co–Pt–Pt–Co, $x(1 - x)^3 J'''$ for Co–Pt–Pt–Pt–Co, etc. Experimental values for the Curie temperature of FCC Co ($T_C = 1394$ K) and a disordered Co–Pt alloy ($x = \frac{1}{2}$) ($T_C = 830$ K) (Sanchez *et al* 1989) can be used to obtain the values $J = 172.2$ meV, $J' = 65.7$ meV and $J/J' = 0.382$. (We have used for simplicity an average value for the spin S of 0.825, and for f a value of 0.695.) Substituting these values in equation (6) gives an expression for the Curie temperature of disordered Co–Pt alloys:

$$T_C = 1394[x + 0.382(1 - x)]. \tag{7}$$

A comparison of this expression with experimental data (Sanchez *et al* 1989, Leroux 1989) shows very good agreement (figure 17). This agreement is consistent with our assumption that the variation in the exchange constants over the range $0 < x < 1$ is small. The good agreement is also evidence that the contributions of long-range interactions via more than one intermediate Pt atom is small. The ratio $J'/J = 0.382$ clearly establishes the importance of indirect Co–Pt–Co interactions.

We now express the energy differences between the magnetic energies δE_i in terms of the interatomic exchange parameters J_1, J_2, J_3, J_4 and J_5 and use a parameter J_0 which is the same for all magnetic structures (this term contains the intra-atomic exchange). The magnetic energies δE are given by

$$
\begin{aligned}
\delta E_F &= -S_F^2(J_0 + 4J_1 + 6J_2 + 8J_3 + 16J_4 + 16J_5) \\
\delta E_{MO(1)} &= -S_1^2(J_0 + 4J_1 + 2J_2 - 8J_3 \qquad\quad - 16J_5) \\
\delta E_{MO(2)} &= -S_2^2(J_0 - 4J_1 + 6J_2 + 8J_3 - 16J_4 - 16J_5) \qquad (8) \\
\delta E_{MO(3)} &= -S_3^2(J_0 - 4J_1 + 2J_2 - 8J_3 \qquad\quad + 16J_5) \\
\delta E_{MO(4)} &= -S_4^2(J_0 \qquad\quad - 2J_2 - 8J_3 \qquad\qquad).
\end{aligned}
$$

From the δE_i values (table 4) it is not possible to calculate all exchange parameters; we obtain the following results: $J_0 = 163.9 + 8J_3$ meV; $J_1 = 9.2 + 4J_5$ meV; $J_2 = 2.9$ meV; $J_3 = 0.8 - J_4 - 2J_5$ meV. In order to be able to calculate values for all exchange constants, we use as additional information the ratio $\alpha = J'/J = 0.382$ (deduced from the ratio of the experimental Curie temperatures of Co and disordered CoPt), and the ratio β of the experimental values of the Curie temperatures of ordered and disordered CoPt (Sanchez *et al* 1989):

$$\beta = T_C(\text{CoPt, ordered})/T_C(\text{CoPt, disordered}) = 710/830 = 0.855.$$

The Curie temperature of ordered CoPt is given by

$$T_C = [2S(S + 1)f/3k_B](4J_1 + 6J_2 + 8J_3 + 16J_4 + 16J_5). \tag{9}$$

The Curie temperature of disordered CoPt ($x = \frac{1}{2}$) is obtained from equation (6) with $J = 12J_1 + 6J_2$ and $J' = 12J_3 + 24J_4 + 48J_5$. From the ratios $\alpha = 0.38, \beta = 0.855$ and the values for δE_i in table 4, we obtain the following values of the exchange constants: $J_0 = 123.2$ meV; $J_1 = 16.2$ meV; $J_2 = 2.9$ meV; $J_3 = -5.1$ meV; $J_4 = 2.4$ meV and $J_5 = 1.8$ meV.

With these parameters it is possible to calculate the Curie temperatures of FCC Co, ordered CoPt and disordered CoPt. The calculated values $T_C = 1718$ K (FCC Co), $T_C =$

1020 K (CoPt, disordered) and $T_C = 870$ K (CoPt, ordered) are in good agreement with the observed values.

For the stability of the non-magnetic structure one would expect $J_0 - 4J_1 + 6J_2 + 8J_3 + 16J_4 - 16J_5 > 0$. This is not the case for the values of the exchange parameters deduced above. Apparently the assumption of constant exchange parameters for all magnetic structures, implicit in equation (8), is not valid for structure MO(2) with a strongly deviating energy.

4. Conclusions

From *ab initio* spin-polarized band-structure calculations of the compounds CoPt, Co_3Pt and $CoPt_3$ it was shown that there is very strong hybridization between the 3d orbitals of Co and the 5d orbitals of Pt. The magnetic moment on the Co and on the Pt atoms are nearly the same in all three compounds. The small moment on Pt is a saturated magnetic polarization of Pt d states induced by the Co spin.

Band-structure calculations were also carried out for several antiferromagnetic spin structures of CoPt. A remarkable feature is that the magnetic moment on Co depends on the type of magnetic ordering considered. In one case the calculations converged to a non-magnetic state. The magnetic energies were analysed in terms of Heisenberg exchange interactions between Co spins. It was shown that it is possible to describe the magnetic properties of Co–Pt alloys quite well with a single set of exchange constants. The *ab initio* band-structure calculations of the energies of ordered magnetic structures are in very good agreement with experimental values. In the Co–Pt alloys it is necessary to take into account direct Co–Co interactions between nearest and next-nearest neighbours. In addition there are strong indirect exchange interactions between Co magnetic moments via one intermediate Pt atom. The strongest of these is an antiferromagnetic 180° Co–Pt–Co interaction J_3. Somewhat weaker are 90° and 120° Co–Pt–Co interactions J_4 and J_5.

Acknowledgments

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